Origin of the ∼150 K Anomaly in LaOFeAs; Competing Antiferromagnetic Superexchange Interactions, Frustration, and Structural Phase Transition

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From first principles calculations we find that the nearest and next nearest neighbor superexchange interactions between Fe ions in LaOFeAs are large, antiferromagnetic (AF), and give rise to a frustrated magnetic ground state which consists of two interpenerating AF square sublattices with M(Fe)=0.48μ_B. The system lowers its energy further by removing the frustration via a structural distortion. These results successfully explain the magnetic and structural phase transitions in LaOFeAs recently observed by neutron scattering. The presence of competing strong antiferromagnetic exchange interactions and the frustrated ground state suggest that magnetism and superconductivity in doped LaOFeAs may be strongly coupled, much like in the high-T_c cuprates.

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The recent discovery of superconductivity at T_c's up to 50 K in layered rare-earth (R) transition metal (Tm) pnictide(Pn)-oxide quaternary compounds ROTmPn (R=La, Ce, Sm, Tm=Mn, Fe,Co, Ni, Pn=P, As)[1, 2, 3, 4] has sparked enormous interest in this class of materials. These are the first non-copper based materials that exhibit superconductivity at relatively high temperatures upon electron ($O_{1-x}F_x$)[1, 2, 3, 4] and hole doping ($La_{1-x}Sr_x$)[5] of their nonsuperconducting parent compounds, just like high-T_c cuprates. Clearly, the understanding of electronic, magnetic, and structural properties of the parent compound LaOFeAs is the key to determining the underlying mechanism that makes these materials superconduct upon electron/hole doping.

Recent theoretical studies suggest conflicting results varying from LaOFeAs being a nonmagnetic metal near a ferromagnetic or antiferromagnetic instability[6, 7, 8] to a simple antiferromagnetic semimetal[10, 11]. From optical measurements and density functional calculations, it was also suggested that LaOFeAs has an antiferromagnetic spin-density-wave (SDW) instability due to Fermi-surface nesting[9]. Experimental studies including resistivity and magnetic susceptibility show a small but very clear anomaly near 150 K in LaOFeAs[1, 9]. The origin of this anomaly has been very recently determined by neutron scattering studies[12, 13]. It has been found that LaOFeAs exhibits an antiferromagnetic long-range ordering with a small 0.35μ_B per Fe moment followed by a small structural distortion[12]. However there is no proposed microscopic theory that explains the origin of the observed stripe-like AF spin decoration and the structural distortion. It is also not clear if the magnetic and structural phase transitions are related to each other. Finally, given the fact that both the cuprates and LaOFeAs exhibit antiferromagnetic ordering, one wonders how strong and what kind of magnetic spin-fluctuations are present in the 2D Fe-square lattice of LaOFeAs.

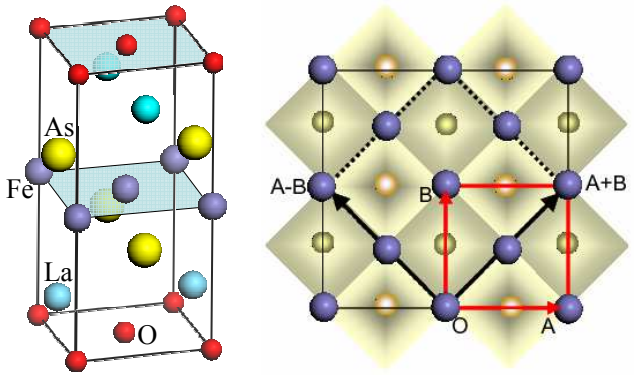

FIG. 1: (color online) (a) The crystal structure of LaOFeAs in space group P4/nmmm with origin choice 1. (b) Top view of the FeAs-plane and the relations between primitive and $\sqrt{2} \times \sqrt{2}$ supercell used in our calculations. The dark and light shaded areas indicate the As atoms below and above the Fe-square lattice, respectively.

In this letter, from accurate all-electron density functional calculations we try to answer some of these questions. We find that both nearest neighbor (nn) and next nearest neighbor (nnn) superexchange interactions between Fe ions in the square lattice are very large, comparable to each other and more importantly they are antiferromagnetic. This forces the Fe spins along the square-diagonal to order antiparallel, resulting two interpenetrating square AF sublattices. Since in this configuration we have one parallel and one antiparallel alignment of the spins along the square axes, the nearest neighbor superexchange interaction is totally frustrated. The system lowers its energy by removing this frustration via a structural distortion that makes the two sides of the square-lattice inequivalent. These results including the magnetic moment of the Fe ions and the degree of structural distor-

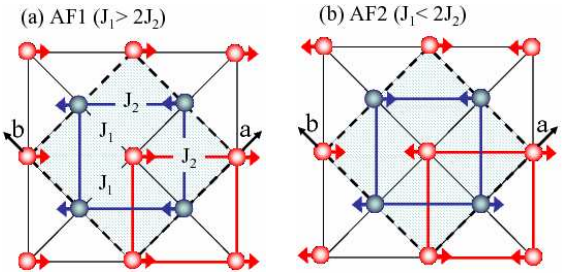

FIG. 2: (color online) Two antiferromagnetic configurations considered in this study. Left panel shows the AF1 configuration where nearest neighbor spins are always aligned antiparallel. Right panel shows the AF2 configuration where the next nearest neighbor spins (i.e.,J_2) are always aligned antiparallel.

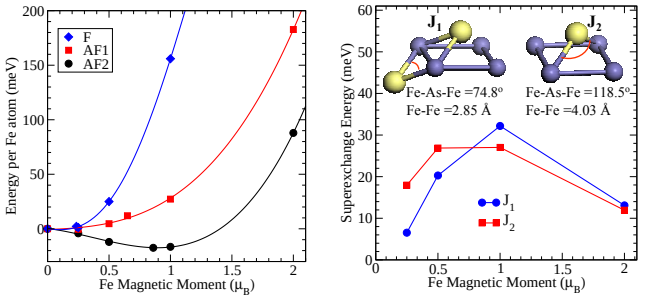

FIG. 3: (color online) (a) The total energy per Fe atom versus magnetic moment for F, AF1 and AF2 spin-configurations, indicating AF2 is the only ground state of the system. (b) The superexchange parameters for nn and nnn Fe ions obtained from the energies of F, AF, and AF2 configurations.

tion, are in excellent agreement with the recent neutron data[12]. Therefore, we have a nice working microscopic theory that explains the details of both the magnetic and structural properties of the undoped parent compound LaOFeAs. Our theory also brings our attention to the presence of the strong competing antiferromagnetic interactions in this class of materials. Even though electron doping seems to destroy the long-range magnetic order, the short range spin fluctuations will be always present and probably play an important role in the superconducting phase, much like the high T_c cuprates. In fact, a theory has been already proposed for the superconductivity mediated by antiferromagnetic spin fluctuations in LaOFeAs[14].

The calculations were done using the full-potential linearized augmented planewave (FP-LAPW) method, one of the most accurate methods available in electronic structure calculations[15, 16]. We also used the ultrasoft pseudo potential planewave (PW) method[17] for cross checking of our results and for phonon calculations. We considered $\sqrt{2} \times \sqrt{2}$ supercell of the primitive cell of LaOFeAs which is shown in Fig. 1. In order to determine the true ground state, we have considered four different cases. These are non-magnetic (NM, i.e., no spin polarization), ferromagnetic (F) and the two different antiferromagnetic spin configurations shown in Fig. 2. The first one of the antiferromagnetic configurations is AF1 where the nearest neighbor spins are antiparallel to each other. The second antiferromagnetic configuraiton, AF2, is shown in Fig. 2b. In AF2 the Fe spins along the square diagonal are aligned antiferromagnetically. The AF2 spin configuration can be considered as two interpenerating simple square AF sublattices (red and blue sublattices in Fig.2b). We note that since each Fe ion is at the middle of a square AF lattice, the mean field at each spin site is zero. Hence one sublattice can be rotated freely with respect to the other sublattice without costing any energy. For this reason the AF2 spin-configuration is fully frustrated. This can be also seen by the fact that for a given square, we have always one parallel (J_1S^2) and one antiparallel ($-J_1S^2$) aligned spin pair, cancelling each others contribution to the total energy. In frustrated magnetic systems, it is known that the frustration is almost always removed by either a structural distortion or by thermal and quantum fluctuations[18, 19]. From the classical energies of AF1 and AF2, one sees that the AF2 spin configuration is stabilized when $J_2 > J_1/2$.

In order to determine which spin configurations among NM, F, AF1, and AF2, is the ground state, we have carried out FP-LAWP total energy calculations for each case. Since in spin-polarized calculations it is very easy to get a local minimum, we followed a different strategy. In our calculations we fixed the magnetic moment per Fe ion and then scan the total energy as a function of Fe-magnetic moment. Our results are summarized in Fig. 3. The zero of energy is taken as the M=0 case (i.e. NM calculation). From Fig. 3, it is clear that LaOFeAs has only one magnetic ground state which is AF2. The Ferro spin-configuration always results the highest energy regardless the Fe-magnetic moment. Similarly AF1 ordering always yields energies higher than the NM case. For the AF2 ordering, we see that the energy minimum occurs near the fixed moment calculation with M=1. Repeating calculations where magnetization is not fixed, we obtained the optimum magnetic moment as M=0.87 μ_B per Fe. As we discuss below in detail, the Fe magnetic moment is further reduced almost by a half when the structure is allowed to distort to remove the magnetic frustration. We note that the magnetic moment obtained from FP-LAPW method is significantly smaller than those obtained from pseudo-potential PW based calculations which give moments around M=2 to 2.5μ_B. We also note that there is no indication of any ferromagnetic interactions present in LaOFeAs which is clear from Fig. 3. In fact, the system prefers to reduce its magnetization to zero if spins are forced to be aligned ferromagnetically. Therefore, we conclude that the main superexchange interactions in LaOFeAs system is anti-

ferromagnetic. The fact that AF2 has lower energy than AF1 indicates that the next nearest neighbor interaction is also antiferromagnetic and satisfies the phase boundary $J_2 > J_1/2$.

In order to gain a better insight into the nature of the superexchange interactions present in Fe-square lattice of the LaOFeAs system, we map the calculated total energies of the F, AF1 and AF2 configurations shown in Fig.3a to a simple Heisenberg like model $H = \sum_{i,j} J_{i,j} M_i M_j$ for a given fixed Fe moment M_i. For fully localized spin-systems this is a perfect thing to do but for the case of LaOFeAs this is only an approximation. Nevertheless, the calculated Js should be a good indication of the superexchagne interactions present in the system. The Fig. 3b shows the J_1 and J_2 obtained from the energies of the F, AF1 and AF2 at given magnetic moment. It is clear that both J_1 and J_2 are quite large and positive (i.e. antiferromagnetic). J_2 is always larger than $J_1/2J$ and therefore AF2 structure is the only ground state for any given moment of the Fe ion. By looking at the superexchange paths for J_1 and J_2 (shown in insets to Fig.3), we notice that the Fe-As-Fe angle is around 75° and 120° for nn and nnn Fe-pairs, respectively. Hence it makes sense that the 2nd nn exchange interaction is as strong as the nn exchange because the angle is closer to the optimum value of 180°. It is quite surprising and also very interesting that there are strong and competing antiferromagnetic superexchagne interactions in LaOFeAs system that result in a totally frustrated AF2 spin configuration. This is very similar to the magnetic ground state of the cuprates where the AF ordered 2D square lattices of the adjacent planes are frustrated[18].

We next discuss the implication of the magnetically frustrated AF2 configuration on the structural distortion recently observed by neutron scattering[12]. It is a common observation that when the system is magnetically frustrated, the frustration is usually lifted by a structural distortion[19]. In the case of LaOFeAs, the frustration is due to the parallel and antiparallel alignment of the spins along the sides of a square. Hence one expects to see a structural distortion which brings the two Fe spins closer to each other while for the other side, they move apart from each other. In fact this is exactly what Cruz *et al.* observed in their neutron scattering experiments. In order to demonstrate the removal of frustration by structural distortion, we calculated the total energy of the AF2 spin configuration as a function of the γ angle as shown in the inset to Fig. 4. When $\gamma = 90°$, we have the original tetragonal cell. Once the γ deviates from 90°, the original $\sqrt{2} \times \sqrt{2}$ structure (shown as dashed line) is no longer tetragonal but orthorhombic (i.e., the cell length along a and b axes are no longer equal). The total energy versus γ plot shown in Fig.4 clearly indicates that the structure is indeed distorted with $\gamma = 91.0°$, which is in good agreement with the experimental value of 90.3°. We note that PW calculations (dotted line) are in excellent agreement with the FP-LAPW method except that the magnetization of the Fe ion comes out very large. From the FP-LAPW method we get M=0.48 μ_B which is in excellent agreement with the experimental value of 0.35 μ_B. We also considered two types of AF2 where the spins along the short axis are aligned parallel or antiparallel. These two configuration are no longer equivalent. From the energies of these configurations we deduce the new superexchange interactions along the a and b directions which are given in Fig. 4. The net energy gain byg the structural distortion is about 12 meV per cell, which is of the same order as the temperature at which this phase transition occurs.

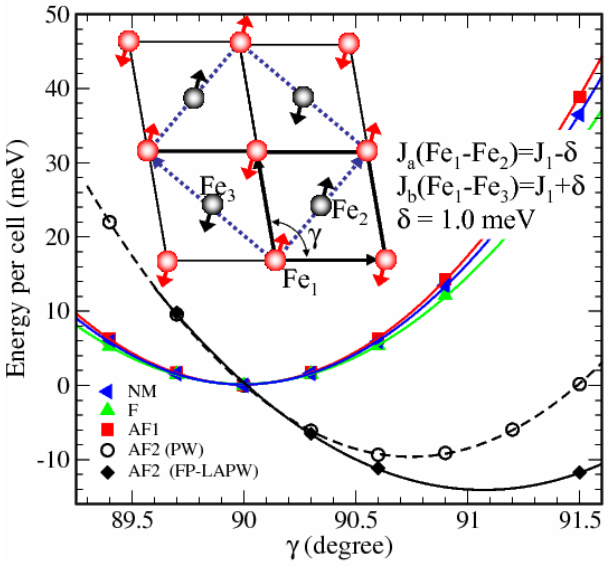

FIG. 4: (color online) The total energy per cell versus the angle γ for non-magnetic (NM), Ferromagnetic (F) and two antiferromagnetic (AF1 and AF2) spin-configurations. Note that only the AF2 spin configuration yields structural distortion. The inset shows that as γ increases, the ferromagnetic aligned Fe ions (i.e., Fe_1-Fe_2) get closer while the antiferomagnetically aligned ions (i.e., Fe_1-Fe_3) move apart, breaking the four-fold symmetry and thus the degeneracy of the d_{xz} and d_{yz} orbitals.

In order to make sure that the structural distortion is driven mainly by frustration removal and not by other effects, we have also calculated total energy versus γ-angle for other spin configurations including the non-magnetic case. We note that for $\gamma = 90°$, the orbitals d_{xz} and d_{yz} are degenerate and therefore one may think that the system is subject to symmetry lowering for reasons similar to those in a Jahn-Teller distortion. However as shown in Fig. 4, we do not see any distortion for any of the NM, F, and AF configurations. Therefore, the experimentally observed structural distortion is due to removal of the frustration generated by the AF2 ordering.

We now briefly discuss the effect of the structural distortion on the electronic structure and the zone center

TABLE I: The symmetries and energies (in meV) of the optical phonons of LaOFeAS in P4/nmm and P2/c phases. The energies of the IR-active modes are taken from Ref.9. The * indicates a significant disagreement! The animations of these modes can be found at http://www.ncnr.nist.gov/staff/taner/laofeas

$\Gamma(P4/nmm) = 2\ A_{1g}$ (IR) + 4 A_{2u}(IR) + 4 E_u (IR) + 4 E_g(R) + 2 B_{1g} (R)												
$\Gamma(P2/c) = 2\ A_g$ (IR) + 4 A_u(IR) + 8 B_g (R) + 8 B_u (IR)												
P4/nmm	P2/c	IR	P4/nmm	P2/c	IR	P4/nmm	P2/c	IR	P4/nmm	P2/c	IR	P4/nmm P2/c IR
E_u 7.3	7.4-7.5	–	A_{2u} 9.9	10.1	12.1	E_g 14.0	14.1-14.2	–	E_g 17.6	17.7-17.8	–	A_{1g} 22.1 22.3 –
A_{1g} 24.9	25.1	–	B_{1g} 26.6	26.9	–	A_{2u} 31.2	31.6	30.9	E_u 33.7	34.0-34.1	33.2	B_{1g} 35.2 35.6 –
E_g 35.6	35.9- 36.1	–	E_u **34.3**	**34.6- 34.7**	**42.0***	A_{2u} 49.1	49.1	53.8	E_g 51.6	51.8-52.6	–	

phonons. The details will be published elsewhere. Fig. 5 shows the electronic density of states before and after the structural distortion with the AF2 ordering in $\sqrt{2} \times \sqrt{2}$ structure. The N(E_F) in both phases are quite small compared to previous calculations in which incorrect AF ordering was considered. It is apparent that the distortion has significant effect both on the N(E_F) and the Fe magnetization. Interestingly, the N(E_F) is doubled while the magnetization is reduced by half due to structural distortion. The increase in the N(E_F) is consistent with the resisitivity measurement which shows that LaOFeAs exhibits metallic behavior after the transition[9]. Finally, we note the existing several sharp Van Hove like kinks in the DOS. In particular the distortion brings one of these kinks just next to the Fermi energy. Hence, with a small electron doping, it is quite possible to increase the N(E_F) significantly. The effect of such electron doping is under study and will be reported elsewhere.

Finally we explain why Dong *et al.* did not see any evidence of the sructural phase transition in their optical IR measurements[9]. From the the symmetry decomposition of the optical phonons in both P4/nmm and P2/c phases (see Table 1), we note that the distortion does not introduce any new IR active modes but rather just splits the doubly-degenerate modes into non-degenerate ones. However the splitting is quite small; the largest is around 0.2 meV. This explains why no new modes appear in the optical measurements after the transition. We also note that the agreement for the energies of the zone center phonons with IR data is not as good as one expects. In particular, the E_u mode observed at 42 meV is calculated to be 35 meV, a significantly lower value. Interestingly, this particular mode has a strong temperature dependence[9]. We checked that the disagreement is not due to anharmonic phonons. The calculated phonons are harmonic unlike those observed in the MgB_2 superconductor[21].We hope that our observation will motivate others to look at the zone -center phonons carefully to understand the discrepency.

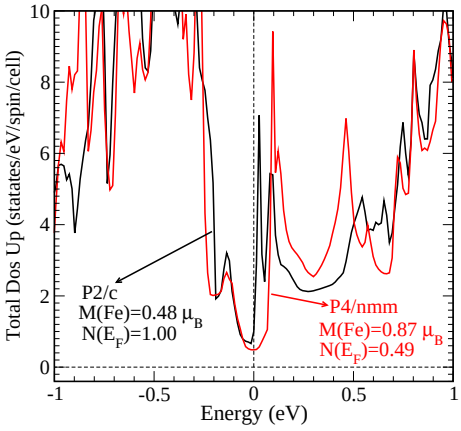

FIG. 5: (color online) The total electronic DOS of LaOFeAs for high (P4/nmm) and low (P2/c) symmetry phases.

In conclusion, we have presented a first-principles study of the superexchange interactions between Fe ions and their effect on the magnetic and structural properties of the parent compound LaOFeO of the newly discovered high temperature superconductor $LaO_{1-x}F_xFeAs$. The competing strong antiferromagnetic exchange interactions and the frustrated ground state suggest that LaOFeAs has many common magnetic properties with the undoped parent component of the high-T_c cuprates.

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